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Growth, Optical, Dielectric and Fundamental Properties of NLO active L-histidinium Perchlorate Single Crystals

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Abstract: Single crystals of L-histidinium perchlorate (LHP) have been grown by slow evaporation solution growth technique. Single crystal X-ray diffraction technique reveals that the crystal belongs to monoclinic system with space group $P2_1$. Some fundamental data such as valance electron, plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal were calculated. The optical absorption spectrum and Second Harmonic Generation (SHG) have been studied to find its linear and Non-linear properties. Dielectric constant measurements were carried out at different temperatures and frequencies.
Keywords: Single crystal, Single crystal XRD, UV-Vis-NIR, Dielectric studies.

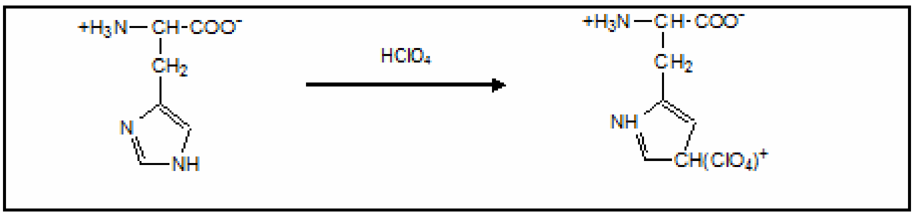
1. Introduction

The importance of amino acid for nonlinear optical (NLO) application lies on the fact that all amino acids contain an asymmetric carbon atom and crystallize in non-centrosymmetric space group. Inorganic crystals have excellent mechanical and thermal stability because they have combined advantage of both organic and inorganic material [1-3]. A typical semi-organic NLO material is formed by combining an organic ion and a counter inorganic ion. Amino acids and inorganic acids are good raw materials to produce semi-organic crystals [4-6].

In this paper, the growth aspects of semi-organic LHP single crystals have been studied and the bulk crystals were grown by slow evaporation solution growth technique. The grown crystals were characterized by single crystal XRD, UV-Vis-NIR, NLO studies. The basic properties has also been studied and reported.

2. Growth of HPC Crystal

L-histidinium Perchlorate crystals (LHP) were grown from aqueous solution by slow evaporation solution growth technique. The starting materials were of high purity L-histidine and Perchloric acid ($HClO_4$). The reaction is given below.



L – histidine **L – histidinium perchlorate**

On the basis of above reaction, a required amount of L-histidine was dissolved in double distilled water. The stoichiometric amount of perchloric acid was slowly added to it. After stirring, the homogenous solution was kept undisturbed. After attaining super saturation large number of tiny LHP crystals were grown by spontaneous nucleation. These seed crystals were used to grow good sized optically transparent crystal for device fabrication. By slow evaporation of the solvent, LHP crystals of size 8x5x1mm^3 were grown in the growth period of 7 days. The as grown crystal is shown in Figure 1.

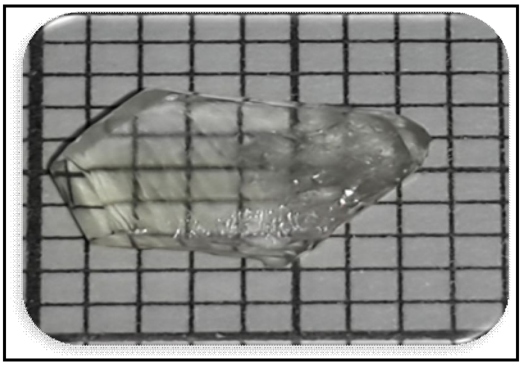


Figure 1. Photograph of as grown LHP crystal

3. Results And Discussion

3.1. X-Ray Single Crystal Diffraction Analysis

Single crystal XRD analysis has been carried out to estimate the lattice parameters, the arrangement and the spacing of atoms in the crystalline material. The crystalline perfection and lattice parameters of the as grown LHP crystals were examined using ENRAF NONIUS CAD-4 single crystal x-ray diffractometer MoKα radiation. From single crystal XRD data it was observed that the grown crystal posses monoclinic crystal system with space group $P2_1$. The lattice parameters are a = 5.07Å, b = 9.2Å and c = 10.41Å, α = γ = 90° and β = 92.32°. Volume of the crystal was 485.564 Å^3 and Z = 2. The single crystal XRD data confirms that the as grown crystal was L-histidinium perchlorate [7].

3.2. Fundamental Parameters of LHP Crystal

The density of LHP crystal was calculated using the relation [8]

$$\rho = \frac{MZ}{N_A abc} \quad (1)$$

Where M is the molecular weight of LPH, molecules per unit cell is Z = 2, N_A is Avogadro's number and a,b and c are the lattice parameters of LHP crystal. The theoretical density is found to be 1.75g/cm^{-3}. The dielectric constant at 1MHz was calculated as ε_∞= 50.2499. The valence electron plasma energy $\hbar\omega_p$ is given by

$$\hbar\omega_p = 28.8\left[\frac{Z\rho}{M}\right]^{\frac{1}{2}} \quad (2)$$

Where Z is the total number of valence electrons, ρ is the density and M is the molecular weight of the LHP single crystal. The plasma energy is given by[8],

$$E_P = \frac{\hbar\omega_p}{(\epsilon_\infty - 1)^{\frac{1}{2}}} \quad (3)$$

and $$E_F = 0.2948\,(\hbar\omega_p)^{\frac{4}{3}} \quad (4)$$

Polarizability α can be calculated using the relation [9],

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_P^2}\right] X \frac{M}{\rho} X\, 0.396\, X\, 10^{-24} cm^{-1} \quad (5)$$

Where S_O is a constant for a particular material, and is given by,

$$S_0 = 1 - \left[\frac{E_F}{4E_F}\right] + \frac{1}{3}\left[\frac{E_F}{4E_F}\right]^2 \qquad (6)$$

The value of α, obtained from equation (6) well matched with Clausius-Mossotti equation, which is given by,

$$\alpha = \frac{3M}{4\pi N \rho}\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right] \qquad (7)$$

Where N is Avagadro number and the calculated fundmental data on the grown crystal of LHP are listed in Table 1.

Table 1. Theoretical data for LHP single crystal

Parameters	Values
Plasma Energy (eV)	23.34
Penn gap (eV)	3.2799
Fermi gap (eV)	19.6635
Polarisability from penn analysis(cm^3)	$5.4x10^{-23}$
Polarisability from Clausius-Mossotti equation (cm^3)	$5.46x10^{-23}$

3.3. UV-Vis-NIR Spectral Analysis

The UV-Vis-NIR spectrum of LHP crystal was recorded in the wavelength range 200 to 900nm using the instrument Varian Cary 5E UV-Vis-NIR spectrophotometer and the spectrum was shown in Figure 2. It was observed that the absorbance was found to be very low in the visible and IR region. This was due to the delocalization of negative charge carriers cloud in charge transfer axis. This is the most desirable property of a NLO material [10]. Low absorbance in the entire visible region indicates that the as grown crystal had less number of inclusions and impurities [11]. The UV-cut off wavelength was around 242nm. The optical band gap of the crystal was determined from Tauc's relation. A plot of variation of $(\alpha h\nu)^2$ versus hν is shown in Figure 3. E_g can be calculated by extrapolating the linear part. The energy gap was of direct type and band gap energy is found to be 5.13eV.

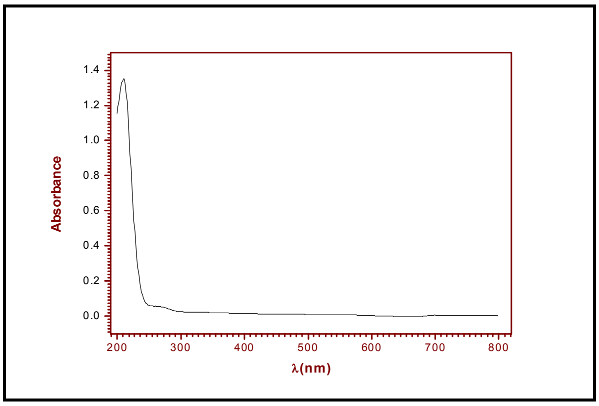


Figure 2. UV- Vis -NIR Spectrum of LHP Crystal

3.4. Nonlinear Optical Analysis

The SHG efficiency of the crystal was examined by Kurtz and Perry powder technique [12] using Quanta ray series Nd:YAG laser emitting first harmonic output of 1064nm with a pulse width of 8ns. The second harmonic signal generated in the as grown crystal was confirmed by the emission of green radiation (λ = 534nm) from it. The measured amplitude of second harmonic green light for LHP was 29.6mJ against 8.7mJ for KDP crystal. Hence the output signal of SHG was found to be 3.4 times greater than that of KDP.

3.5. Dielectric Studies

Dielectric measurements were done with carefully cut and polished LHP crystal of size l = 0.532cm, b = 0.45cm and d = 0.32cm with the instrument HIOKI 3532 – 5- LCR HITESTER. The capacitance and loss tangent were measured in the frequency range 100Hz to 1MHz in the temperature range of 313K to 403K.

The dependence of dielectric constant with frequency was shown in Figure 4. At low temperatures (313K), the dielectric constant (ε') decreases from 100.62 to 50.7 whereas in the high temperature (403K), the dielectric constant (ε') decreases from 105.07 to 50.7 in the frequency range 100Hz to 1MHz. Rate of decrease in dielectric constant was higher at high temperature and lower at low temperature ranges and it decreases with the increase in frequency in all temperature ranges. At higher frequencies, the dielectric constant was almost same for all temperature ranges due to the inability of electric dipoles to follow the fast variation of alternating applied electric field, which is the expected behaviour in most of the dielectric materials [13].

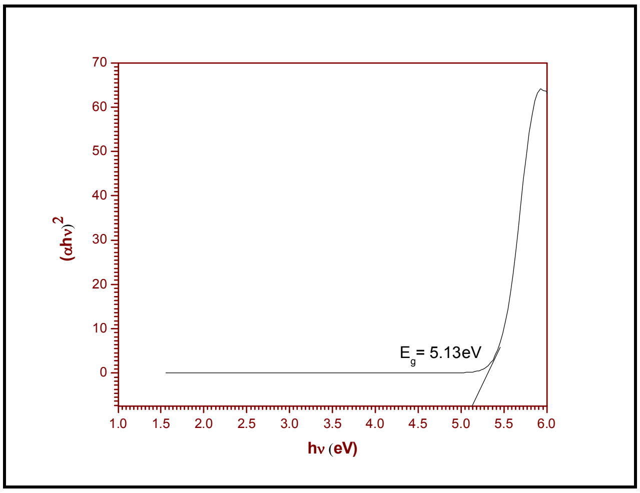


Figure 3. Tauc's Plot of LHP Crystal

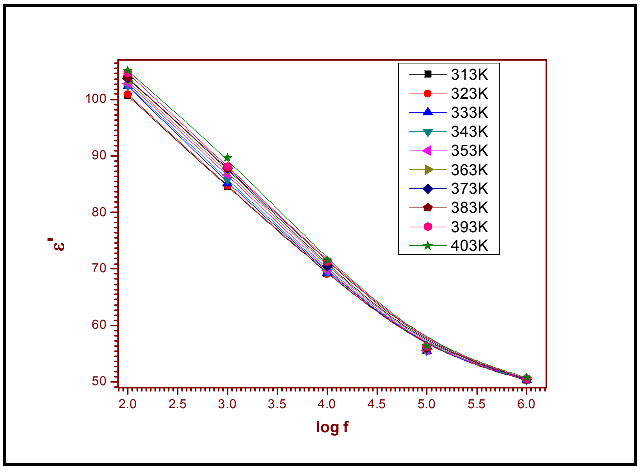


Figure 4. Variation of ε' with log f for LHP Crystal

4. Conclusion

A Non Linear Optical single crystal, LHP was successfully grown by slow evaporation method. Single crystal XRD method reveals the crystalline nature of the as grown crystal and the structure is observed to be monoclinic. Optical transparency of the crystal is analyzed from UV-Vis-NIR spectrum. Optical band gap energy of the crystal is found to be 5.13eV. NLO property is confirmed by kurtz powder SHG test. The NLO efficiency is 3.4 times of KDP. Dielectric studies reveal its normal nonlinear optical behavior. Thus preliminary studies suggest LHP can be used for photonics device fabrication.

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